

SpecFUELTM

Additional Comparative Information For Pet Coke and Wood/Biomass

INTRODUCTION

On March 16, 2012, Waste Management (WM) submitted a request for a comfort letter determination that SpecFUEL is a non-waste fuel pursuant to the final rule entitled "Identification of Non-Hazardous Secondary Materials that are Solid Waste", published at 86 Fed. Reg. 15456 (March 21, 2011) and codified at 40 CFR Part 241 (the "NHSM Rule"). WM's submission provides a demonstration that SpecFUEL meets the legitimacy criteria set forth in 40 CFR §241.3(d), including that SpecFUEL contains contaminants at levels comparable in concentration to those in traditional fuels (coal, wood, fuel oil and petroleum coke). In follow-up communications in September 2012, EPA requested that WM provide further information with respect to antimony and fluoride as constituents in SpecFUEL as compared to traditional fuels. WM submitted the requested information on September 7, 2012. On October 17, 2012 WM provided information to respond to additional questions raised by EPA for coal and wood/biomass. That information supported comparability of antimony, fluoride and organic HAPs, with specific emphasis on the plastizer bis(2-ethylhexyl)phthalate (DEHP). WM also provided information supporting the use of supplementary coal information for making contaminant comparisons among secondary material fuels and coal.

Since the October 17, 2012 submittal EPA indicated that a similar analysis of antimony, fluorides, organic HAPs and DEHP in petroleum coke (pet coke) and wood/biomass as compared to SpecFUEL would likely be needed to include energy recovery units designed to burn pet coke and wood/biomass in the comfort letter. Based on the Agency's follow up comments, WM is providing the information below to demonstrate that SpecFUEL is comparable to pet coke and wood/biomass.

DISCUSSION

1. Petroleum Coke – Metals and Halides

In the submittal on March 16, 2012 to EPA, WM stated the following.

This summary shows that for nitrogen and sulfur, SpecFUEL has lower concentrations of these contaminants than coal, wood/biomass, fuel oils, and coke. Total halogens (chloride, bromide, and fluoride) are lower in SpecFUEL than in both coal and wood/biomass. Organic compound concentrations in SpecFUEL are either far lower than those of traditional fuels or data for traditional fuels (wood/biomass and pet coke) are not available for comparison.

EPA's November 29, 2011 traditional fuel data set provided no information for pet coke. WM conducted additional research on pet coke and used the following data for its March 16, 2012 submittal.

- 1) EPA Letter "Contaminant Concentrations in Traditional Fuels: Tables for Comparison," November 29, 2011
- 2) EPA-OSWER letter to Joseph Knapik- International Paper Products Corporation. (NHSM comfort letter issued October 5, 2011)
- 3) Loutfi, H., Harriz, T. "Mill Use of Petcoke as an Alternative Lime Kiln Fuel to Reduce Energy Costs," 2006 TAPPI Forum on Energy
- 4) Cabral, R., Damo, T., Kosak, R., Patel, V., Vahanwala, L. "Syngas Production from Petroleum Coke Gasification." Presentation on January 24, 2011.6
- 5) United States EPA: National Risk Management. "Control of Mercury Emissions from Coal-Fired Electric Utility Boilers: Interim Report Including Errata Dated 3-21-02." Prepared for Office of Air Quality Planning and Standards.
- Sietronics Pty Limited Coal and Coke Laboratory Analyses. Section 24.1 and 24.9. http://www.sietronics.com.au/mbh

Unfortunately, WM was unable to find information on organic HAP concentrations in pet coke. To augment our original analysis, WM has conducted its own laboratory analysis of pet coke and additional literature research to develop the following tables to demonstrate that contaminants in SpecFUEL are comparable to those in pet coke.

¹ Tables for Comparison" dated November 29, 2011 (the "Contaminant Comparison Guidance") posted on EPA's website at http://www.epa.gov/osw/nonhaz/define/pdfs/nhsm_cont_tf.pdf.)

The first table shows the comparison of pet coke to SpecFUEL for metals and halides. The second table shows a comparison of pet coke and wood/biomass to SpecFUEL for organic HAPs.

Metals Comparison

In data previously submitted by WM, metals were classified into two groups; total metals (TM) and low volatile metal (LVM), for purposes of contaminant comparisons. The TM and LVM 90% UPL concentrations in SpecFUEL are 167.3 mg/Kg and 124.2 mg/Kg, respectively, compared to the maximum TM and LVM concentrations identified in the augmented pet coke database of 1597.3 mg/Kg and 1471.8 mg/Kg, respectively (see Table 1 for references). Clearly, SpecFUEL metals content is significantly lower than the metals concentrations found in pet coke data.

WM obtained samples of pet coke commercially available in the U.S. and contracted with NELAC-certified laboratories to have them processed and analyzed. WM also identified data from pet coke being combusted in Europe from a 2004 article published in a well-regarded, peer-reviewed journal "Environmental Research." Petroleum coke is accessed and used by manufacturing facilities, such as cement kilns, on a worldwide basis so the pet coke combusted in Europe has a high probability of being used in the U.S. as a traditional fuel. We further note that EPA used European traditional fuel data in the Nov 29, 2011 data set, (Energy Research Centre for the Netherlands, Phyllis Biomass database. http://www.ecn.nl/phyllis.) As WM mentioned in its previous comments on October 17, 2012, these fuels could be combusted as fuel in numerous Clean Air Act permitted sources in the U.S. potentially subject to NHSM and CISWI rules.

Halides Comparison

WM also provides halides data in Table 1. An EPA report prepared by OAQPS and used as a reference in the Boiler MACT supplied halides data for pet coke.² The 90% UPL for halides in SpecFUEL is 3416 mg/Kg compared to the high value in pet coke of 3007.5 mg/Kg. Based on contaminant comparisons approved by EPA for other secondary materials, WM believes that the halides data are comparable. In comparison, EPA found cadmium to be comparable for C&D wood at 0.17876 ppm versus coal at 0.06510 ppm (a difference of 175 percent).³ EPA also

² National Risk Management. "Control of mercury emissions from coal-fired electric ulility boilers: interim report including errata dated 3-21-02" Prepared for OAQPS. Table A-10.

³ Fed. Reg. Vol 76, No. 54, page 15845, Table 1.

determined chlorine to be comparable at 56.0 lb/billion btu in C&D wood versus coal at 46.0 lb/billion btu (a difference of 22 percent).

Table 1. SpecFUEL Comparison to Pet Coke – For Metals and Halides.

		SpecFUEL *di results reported as moisture free *di results pooled from all 7 samples				od and	Biomass	Petroleum Coke			
		Range		90% UPL	Range			Range			
	Average	Low	High	Results*	Low	High	Reference	Low	High	Reference	
Metals (mg/kg)						-		-			
Antimony (HAP)	29.10	16.90	51.40	46.2	n.d.	26	(1)	0.14	3	(2) (4)	
Arsenic (HAP)	0.61	0.61	0.61		n.d.	298	(1)	1.08	17.3	(3),(4)	
Beryllium (HAP)					n.d.	32	(1), (2)	0.05	0.05	(3),(4)	
Cadmium (HAP)	0.60	0.34	1.37	1.139**	n.d.	17	(1)	n.d.	n.d.	n.d.	
Chromium (HAP)	15.17	10.30	20.60	23.34**	n.d.	340	(1)	1.35	114	(3),(4)	
Cobalt (HAP)	1.09	0.78	1.38	1.4	n.d.	213	(1)	0.41	0.45	(3)	
ead (HAP)	21.69	12.30	45.00	40.4	n.d.	340	(1)	0.71	125	(3),(4)	
Manganese (HAP)	38.49	34.00	47.20	46.0	n.d.	15800	(1)	5.6	550	(3),(4)	
Mercury (HAP)	0.20	0.05	0.28	0.3	n.d.	11	(1)	0.001	0.5	(4)	
lickel (HAP)	2.86	1.72	7.24	7.24***	n.d.	540	(1)	52	787	(3).(4)	
elenium (HAP)	1.15	1.03	1.28	1.3	n.d.	66	(1), (2)	n.d.	n.d.	n.d.	
otal Low Volatile Metals (mg/kg) ⁶	87.31	64.31	128.43	124.2	n.d.	17249	12//(2/	n.d.	1471.8	n.u.	
otal Metals (mg/kg)	110.95	78.03	176.35	167.3	n.d.	17673.1		THE RESIDENCE TO SERVICE THE PERSON NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TWO IS N			
lalides		10.00	210.00	A	11.4.	A/0/3.1		n.d.	1597.3		
romide (mg/kg)	6.27	4.90	6.80	6.8***		7		n.d.	63	(2) (4)	
hloride (mg/kg)	2032.86	1840	2250	2250***	n.d.	5400	(1)	7	3000	(3),(4)	
luoride (mg/kg)	891.57	585	1070	1159	n.d.	490	(1), (2)	1.1	1.2	(5)	
otal Halides (mg/kg)	2930.70	2429.90	3326.80	3416	0	5890	(4), (2)	8.1	3007.5	(3)	
All 90% UPL Results reported as Normal			-	A		3450		0.1	3007.5		
* 90% UPL Result reported as Lognormal						T			T		
** 90% UPL Result Non-Parametric								_			
.d. = Non-Detect											
- = No Data											
A - Not applicable; PAH's accounted for in testing o	f Volatile Compoun	ds and Sem	·Volatile C	ompounds							
esources:					-		-	-	-THE SAME		
EPA Letter "Contaminant Concentrations in Traditi	onal Fuels: Tables f	or Comparis	on." Noven	sber 29, 2011.							
EPA Letter to Joseph Knapik-International Paper P	roducts Corporation	n. October 5	, 2011								
Obtained Pet Coke Sample Analyzed by a NELAC C	ertified Laboratory										
Bosco, M.L., et al. "Case study: Inorganic pollutant:											

2. Organic HAPs - Wood/biomass and Pet Coke

WM provides in Table 2, a comparison of organic HAPs in SpecFUEL to levels found in wood/biomass and pet coke. Similar to previous WM submittals, total organic HAPs are compared below as the sum of all volatile and semi-volatile organic HAPs.

Table 2. SpecFUEL Comparison to Pet Coke and Wood/Biomass-For Organic HAPs.

/olatile Compounds (µg/kg) Jenzene (HAP) Sthyl benzene (HAP) Formaldehyde (HAP) sopropylbenzene (HAP)	Average	Ra	nge High	90% UPL Results*		inge	2.6	Ra	nge	
Benzene (HAP) Ethyl benzene (HAP) Formaldehyde (HAP)			100			1	0.6	110		
Benzene (HAP) Ethyl benzene (HAP) Formaldehyde (HAP)				nesuits	Low	High	Reference	Low	R	
Ethyl benzene (HAP) ormaldehyde (HAP)										
ormaldehyde (HAP)										
	45.4	38.0	54.8	54.5			10.7	**		
	5029	3300	6300	6900	1600	27000	(1)			
	17.4	12.2	24.6	23.8	1000		127	**		
n,p-Xylenes (HAP)	59.9	44.0	85.6	83.6		4.1				
o-Xylenes (HAP)	33.2	20.2	49.6	49.0				4-		
Total Xylenes			-3.0	73.0		**		**		
Methylene chloride (HAP/OH)	55.3	27.4	143.0	111.6**	144	-		**		900
-Hexane (HAP)	33.3		143.0	111.0	**					
Phenol (HAP)			-		- ::		988			-
tyrene (HAP)	313.0	240.0	422.0	405.1			- "			
etrachloroethylene (HAP/OH)	8.00	8.00	8.00	403.1				3 3		
oluene (HAP)	35.63	17.80	89.00	70.04**		**	7**	**	**	**
otal Volatile Compounds (µg/kg)	5596.33	3707.60	7176.60	7698	1600					
emi-Volatile Compounds (µg/kg)	3330.33	3/0/.00	/1/6.60	7698	1600	27000		**		
-Methylnaphthalene	n.d.	n.d.	n.d.	n.d.		-		n.d.	1680	(2)
-Methylnaphthalene	n.d.	n.d.	n.d.	n.d.	- 12	**	-	4240	4730	(2)
nthracene	n.d.	n.d.	n.d.	n.d.				n.d.	1990	(2)
enzo(alanthracene	n.d.	n.d.	n.d.	n.d.	22			6780	8360	(2)
enzo(a)pyrene	n.d.	n.d.	n.d.	n.d.	- 55%	-		6530	8160	(2)
enzo(g,h,i)perylene	n.d.	n.d.	n.d.	n.d.				5730	7290	(2)
is(2-ethylhexyl)phthalate (HAP)	731571	240000	1410000	1423994			257	n.d.		(2)
hrysene	n.d.	n.d.	n.d.	n.d.	2			8720	n.d. 10900	n.d.
ibenz(a,h)anthracene	n.d.	n.d.	n.d.	n.d.						(2)
ndeno(1,2,3-cd)pyrene	n.d.	n.d.	n.d.	n.d.				3780	4880	(2)
aphthalene (HAP)	226.57	101.00	566.00	491.9**		**		2010	2390	(2)
henanthrene	n.d.	n.d.	n.d.		**	••	**	2040	2280	(2)
yrene	n.d.	n.d.	n.d.	n.d.		**	-	3380	4200	(2)
otal Semi-Volatile Compounds (µg/kg)	731798	240101	1410566	n.d.				4530	5720	(2)
olycyclic Aromatic Hydrocarbons (µg/kg)	/31/98	240101	1410366	1424486		**		47740	62580	-
6-PAH	NA	NA	NA	NA				***		
AH (52 extractable)	NA NA	NA NA	NA NA	NA NA			-	NA	NA	NA
otal Polycyclic Aromatic Hydrocarbons (µg/kg)	IVA	INA	IVA	NA	-			NA	NA	NA
otal Organic HAPs (mg/kg)	737	244	1418	1432	1.6	27.0		47.7	62.6	
otal Organic HAPs (mg/kg) - Without DEHP	5.8	3.8	7.7	8.2	1.6	27.0		47.7	62.6	

Organics in Wood/Biomass

As seen in Table 2, formaldehyde (27 ppm) is the only organic HAP constituent reported by EPA/OAQPS in its database for traditional wood and biomass. While EPA/OAQPS database does not provide additional organic HAP data, other than formaldehyde for wood/biomass, EPA

has data demonstrating that traditional wood does have VOCs within the wood itself, and that this amount can be as high as 20,000 ppm.⁴ Traditional biomass contains numerous organic compounds in a solid/liquid matrix which can potentially emit/volatilize minor fractions of VOCs, including listed hazardous air pollutants, under standard temperature and pressure. By increasing temperature and/or the pressure, but not to the point of combustion, traditional biomass can further emit/volatilize such VOCs in increasing fractions. Given the highly complex nature of the organic compounds which comprise traditional wood, identification of the series of chemical reactions for this process continues to generate extensive research.

In addition, there are ample datasets on the emissions of VOCs from the process of drying, but not combusting, traditional wood. While most drying is done prior to processing the wood into products, some traditional wood fuels are dried prior to combustion for various reasons, e.g., reduction of hauling costs. A good example of such process is the Green Circle Bioenergy plant in Florida which dries virgin southern pine prior to shipment to Europe. After drying and pelletizing, these pellets are sold as a carbon-neutral combustion source (per EU cap-and trade) to power production facilities in Europe. 5 The organic content of such traditional fuel has been shown to result in significant organic HAPs. For example, according to scientists from Oregon State University, ponderosa pine wood dryers emit between 1.6 and 3.0 pounds of VOCs per thousand board feet (mbf) (3330 lb⁶), or 480 to 900 part per million mass basis, depending on the temperature of the dryer. The portion of measured VOC HAPs (volatile organic compound that is a hazardous air pollutant per 40 CFR 63) (study includes methanol, formaldehyde, acetaldehyde, propionaldehyde, and acrolein) from these ponderosa pine wood dryers ranged from 0.0833 to 0.189 lb/mbf (25 to 57 ppm mass basis). Similar measurements show clean wood dryers generating 0.96 pounds per oven dried ton of the VOC HAP, methanol (i.e., 0.048 percent (480 ppm-mass methanol per mass of wood) methanol per ton of dried wood). ⁸ Based on this process knowledge, we believe that the organic HAPs content of traditional wood is much greater than is recognized within the EPA-OAQPS database and any comparison of secondary material fuel to traditional wood/biomass should reflect the intrinsic organic HAP content in the virgin wood prior to drying the wood to prepare it for use in products or as fuel.

⁸ EPA, AP-42, 5th edition, Table 10.6.3-3, http://www.epa.gov/ttn/chief/ap42/ch10/final/c10s0603.pdf

⁴ See EPA-HQ-RCRA-2008-0329-1866 (AF&PA data on organic contaminants in traditional fuel showing that Virginia pine can contain 2% turpentine, which is a VOC).

⁵ http://www.greencirclebio.com/index.php

⁶ AP-42, Appendix A, 40 lb/ft3 – based on density of pine, (1 mbf = 83.3 ft3)

Milota and Mosher, Emissions of hazardous air pollutants from lumber drying, Forest Products Journal, July/August 2008, Vol. 58, No. 7/8, at 52. Available at http://www.deq.idaho.gov/media/591021-milota_mosher_emissions_study.pdf

Organics in SpecFUEL

Table 2 shows the Total Organic HAPs with and without the HAP, bis(2-ethylhexyl)phthalate, or DEHP. DEHP is a chemical that is mass produced and used in plastics, resins, consumer products and building materials. In general, phthalates are used as plasticizers to enhance the durability and flexibility of plastics and other polymers. DEHP is synthesized through bulk manufacturing processes, and the resulting production air releases at these manufacturing facilities are the reason that EPA has listed DEHP as a HAP, not because DEHP emissions are associated with combustion sources.

The presence of DEHP in SpecFUEL is not unexpected and would be anticipated in broad range of secondary materials sourced from post-consumer products or industrial or commercial waste. Therefore, DEHP should not be present in traditional fuel materials, and direct comparison of DEHP to traditional fuels must consider that petroleum-synthesized plastic materials are not present in pet coke or wood/biomass.

As such, a group comparison was again utilized for the contaminant comparison of this HAP, consistent with the NHSM Reconsideration Rule. A group comparison of all organic constituents (HAPs) was made. This compilation of HAPs includes volatile organic compounds, semi-volatile organic compounds and polycyclic aromatic hydrocarbons (PAHs). While the NHSM Reconsideration Rule proposal states that total PAHs may be a distinct group (see Table 8 at 76 Fed. Reg. at 80479 and 80480), the Agency also makes clear that persons can use other approaches that they can show are technically reasonable (see 76 Fed. Reg. at 80477). We believe PAHs can and should be grouped with the other organic compounds, since PAHs are a compilation of organic compounds. In fact, according to the Laumann et al. (2011) document used by EPA for the reporting of PAHs in the Contaminant Comparison Guidance, the PAH values used in this document included Naphthalene, which is defined by EPA as a semi-volatile organic compound (SVOC) in the NHSM Reconsideration Rule. See 76 Fed Reg. at pgs 80479 and 80480. As such, for the SpecFUEL pollutant comparison, the total grouping included all measured organic HAPs.

As seen in the attached table, the SpecFUEL 90% UPL results yielded a total organic HAPs concentration of 1,432 mg/kg of which 99.5 percent is DEHP. Not considering DEHP, SpecFUEL is very comparable to both wood/biomass and pet coke. SpecFUEL without DEHP has 8 ppm of total organic HAPs in comparison to pet coke at 62.6 ppm and wood/biomass at 27 ppm.

⁹ Stiles, R., Yang, I., Lippincott, R.L., Murphy, E., Buckley, B. "Potential Source of background contaminants in solid phase extraction and microextraction." Journal of Separation Science. 30:1029-1036. (2007).

As WM raised in its October 17, 2012 submission comparing antimony, fluoride and DEHP in SpecFUEL to levels found in coal, additional factors may also, and should also, be considered regarding DEHP in SpecFUEL. EPA's definition of "contaminant" in the NHSM Rule includes (in pertinent part) "any constituent in non-hazardous secondary materials that will result in emissions of the air pollutants identified in Clean Air Act section 112(b) or the nine pollutants listed under Clean Air Act section 129(a)(4) when such materials are burned as a fuel...." 40 CFR §214.2. Through the Reconsideration Rule, EPA has proposed to add several elemental contaminants that are likely to cause the formation of HAPs during combustion. See 76 Fed. Reg. at 80471. EPA's preamble language in the NHSM Rule and in the Reconsideration Rule have addressed whether the contaminant comparison should be made on the basis of HAP constituents in the non-hazardous secondary material, or on the emissions resulting from the combustion of that material. EPA has clarified in the Reconsideration Rule proposal its view that it is the constituents prior to combustion that must form the basis of the contaminant comparison. Id. However, EPA has not addressed the circumstance that may be confronted with certain constituents, such as DEHP, that may be present at certain levels prior to combustion, but that would be effectively destroyed in the combustion process, and would not lead to the formation of other HAPs. In this circumstance, the existing definition of "contaminant" should be controlling, and would dictate that the presence of a HAP constituent that is not otherwise capable of comparison, and that would not ultimately be emitted or lead to the emissions of other HAPs, would not prevent a favorable comparison with traditional fuels.

Expanding on the case of DEHP and its potential for release or its potential to cause the formation of other HAPs during combustion, the University of Dayton Research Institute (UDRI) currently maintains and updates a database, supported and frequently referenced by EPA, ranking numerous organic compounds based on their thermal stability under oxygen-starved conditions. This ranking lists the group of organics in order of their potential for relative destruction efficiency. Towards the top of the list, a large portion of polycyclic aromatic compounds (PAHs) can be found. ¹⁰ And, as shown in EPA's November 29, 2011 traditional fuel data set, PAHs strongly control the amount of total organic HAPs present in coal.

When introducing this ranking system to petroleum coke and its HAPs, the same trend seen in coal can be seen for pet coke. As shown in Table 2, a majority of the HAPs present in the petroleum coke sample analyzed for the purposes of this project fell into the category of PAHs (Benzo(a)anthracene, Benzo(a)pyrene, Benzo(g,h,i)perylene, Chrysene,

¹⁰ EPA/625/6-89/019, Guidance on Setting Permit Conditions and Reporting Trial Burn Results, Volume II of the Hazardous Waste Incineration Guidance Series, Table D-1. Newest compilation of ranking attached to document.

Dibenzo(a,h)anthracene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, and Pyrene). Utilizing the data from the analysis, this equates to approximately 43.5 ppm which is a majority of total organic HAPs that are PAHs and difficult to combust. This number is once again significantly higher (530 percent greater) than the total organic HAP concentration (not including DEHP) of 8.2 ppm for SpecFUEL.

In fact, in this EPA ranking system benzene is ranked third on this list of 320 organic compounds and benzene, as defined by EPA, has a potential concentration of 38 ppm in coal (460 percent higher than total organic HAPs in SpecFUEL less DEHP). While DEHP is ranked on this list, it is ranked 278th. At this ranking, it was determined that DEHP can achieve 99% destruction at 2 seconds of gas-phase residence time at a temperature of 370 °C – less than half the temperature required for destroying PAHs and formaldehyde. These conditions are easily achieved in combustion processes where petroleum coke and biomass are common fuel sources. Accordingly, on a quantitative basis, the presence of DEHP in SpecFUEL is less significant from an emissions standpoint than the organic HAPs found in coal and petroleum coke, and therefore should not prevent a favorable contaminant comparison for organic HAPs.

SUMMARY

While comparisons were made under certain groupings of data, this grouping technique was necessary given the limited data that exist for some traditional fuels such as pet coke. As previously emphasized, EPA's November 29, 2011 traditional fuel data set did not include petroleum coke data. When additional sources for potential data for comparison were sought, the limited available data required WM to follow through with an independent study and analysis carried out by a NELAC-certified laboratory to develop petroleum coke data. This was also the case for wood/biomass, where formaldehyde was the only reported HAP for comparison. Due to these limited datasets, WM had to pursue various groupings to demonstrate SpecFUEL's "contaminant comparison." WM believes that when there is a limited amount of representative contaminant data for some traditional fuels, expanded or alternative methods for evaluation may be appropriate, as set forth herein, in conducting contaminant comparisons that evaluate available data. EPA has stated that as additional traditional fuel data becomes available that data can be used to revise the comparison. We encourage EPA to disseminate any new traditional fuel information it has obtained.

Based on the foregoing and previously submitted information, WM believes that the comparison between contaminant concentrations present in SpecFUEL, and those present in traditional fuels of wood/biomass and pet coke, demonstrate that SpecFUEL meets the "contaminant comparison" legitimacy criterion under the NHSM Rule.

ATTACHMENT

EPA Ranking of Thermal Destruction Efficiency

EPA/625/6-89/019

Maintained by Dr. Phil Taylor, UDRI

Updated on May 7, 2012